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## CHALLENGES FOR THE DEVELOPMENT OF INKJET PRINTED $\text{Cu}_2(\text{Zn},\text{Sn})(\text{S},\text{Se})_4$ THIN FILM SOLAR CELL

Ahmed Ennaoui<sup>1,4</sup>, Xianzhong Lin<sup>2</sup>, Jaison Kavalakkatt<sup>2</sup>, E. M. Vinod<sup>1</sup>, Reiner Klenk<sup>2</sup>, Martha Ch. Lux-Steiner<sup>2,3</sup>

<sup>1</sup>Qatar Environment and Energy Research Institute (QEERI), Hamad Bin Khalifa University, Qatar Foundation, P.O. Box 5825, Doha, Qatar

<sup>2</sup>Institute for Heterogeneous Material Systems, Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

<sup>3</sup>Free University of Berlin, Kaiserswerther Str. 16-18, 14195 Berlin, Germany

<sup>4</sup>College of Science and Engineering, Hamad Bin Khalifa University, Qatar Foundation, P.O. Box: 5825, Doha, Qatar

### Abstract

Inkjet printing technique is a material-conserving technique, which can greatly reduce the production cost by reducing the wastage of materials during the deposition. Additionally, this method can be easily adapted to Roll-to-Roll processing for large-scale application. The most challenging issues that remain open for multi-component system such as  $\text{Cu}_2\text{ZnSn}(\text{S}_x\text{Se}_{1-x})_4$  (CZTSSe) are: (1) Formulation of long-term stability raw material ink and (2) Optimization of electronic and electrical properties for high efficiency solar cell. We developed two different methods for ink formulation. The first one is based on preparation of nanoparticles such as ZnS, SnS and  $\text{Cu}_3\text{SnS}_4$ . The second method consists of metal salt precursors dissolved in organic solvents. We use metal salt solutions containing Cu, Sn, Zn and S precursors dissolved in dimethyl sulfoxide (DMSO) to prepare the ink. We used two deposition techniques (spin coating, inkjet printing) for the preparation of absorber layers. Both methods lead to the production of kesterite films. However the metal salt based ink is well adapted to inkjet printing and the resulting solar cells with glass/Mo/CZTSSe/CdS/ZnO structure show total area (0.5 cm<sup>2</sup>) efficiency of 6.4 %.

Keywords: *Inkjet printing, kesterite, thin film solar cell*

### 1. Introduction

Kesterite  $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$  (CZTSSe) has emerged as a promising candidate for solar energy conversion. The optical band gap of this material can be tuned between 1.0 eV and 1.5 eV by changing  $[\text{S}]/([\text{S}]+[\text{Se}])$  ratio. Wang et al., have developed a solar cell with record efficiency of 12.6% obtained for CZTSSe absorbers from hydrazine-based solution [1]. However the fabrication process suffers from certain safety hazards due to the use of explosive and toxic hydrazine solvent. Previously, we have shown that CZTSSe thin film absorbers can be formed by annealing spin coated in-house formulated ZnS, SnS and  $\text{Cu}_3\text{SnS}_4$  (CTS) nanoparticle (NP) inks [2-5]. Cao et al. have fabricated CZTSSe based solar cells with efficiency up to 8.5 % by using a similar binary and ternary chalcogenide nanoparticle as precursors to prepared CZTSSe absorber [6]. Another way is to use CZTS quaternary nanoparticles as precursors to fabricated CZTSSe thin films [7, 8]. This approach has led to an efficiency of 9.0 %. However, the nanoparticle (NP) synthesis process is time consuming and requires complicated steps. Moreover, long chain organic ligand is required to prevent the agglomeration of the nanoparticles during the synthesized process, which is difficult to be removed after thin film processing. Therefore, a ligand-exchange process to minimize the amount of carbon in the layers may be needed. Although the ligand exchange can reduce the carbon content in the layers, the resulting absorbers

still containing large amount of carbon left near the back contact after the annealing step, which limit the performance of the solar cell device. A simple alternative approach developed by Ki et al., is based on Cu, Zn, and Sn precursors dissolved in DMSO leads to efficiency of 11.8% obtained by annealing the spin-coated Cu-Zn-Sn-DMSO solution [9, 10]. It has been reported that sodium has a positive influence on the morphology as well as electronic properties of CZTSSe absorbers, thereby enhancing the solar cell performance [11].

## 2. Experimental

### 2.1. Sample preparation

NP inks were prepared from ZnS, SnS and Cu<sub>3</sub>SnS<sub>4</sub> (CTS) NP precursors in certain ratio mixed with oleylamine (solvent) and 1-dodecanethiol (capping agent) [5]. This mixture was heated to 130°C with 10 °C/min and held at this temperature for 30 minutes. Thereafter, the mixture was further heated to higher temperature (200 °C-250°C) and stayed at this temperature for certain time to allow the growth of the NP. After cooling room temperature, the NP were precipitated by addition of excessive ethanol or acetone followed by centrifugation. The precipitated NP was dispersed in toluene or 1-hexanthiol to formulate the ink. Thin films were deposited by spin coating of using the NP inks. The residual solvents and organic surfactants surrounding the NP were removed by heating at 170 °C and 350 °C respectively for 2 minutes. It should be noted that a ligand exchange process is carried out with 0.04 M (NH<sub>4</sub>)<sub>2</sub>S methanol solution for the sample cooled to RT from 170 °C. Thick films are obtained by repeating the spin coating and intermediate annealing at 350 °C. The processed CZTS NP film is further annealed at 580 °C for 25 minutes in Se atmosphere to form CZTSSe absorbers. The chemical composition of the absorber layer can be tuned by adjusting the ratio of NP precursors. It is also reported that the CZTSSe based SC performance is strongly dependent on the ratios of Cu/(Zn+Sn) and Zn/Sn [5]. The chemical reaction leading to the formation of CZTSSe can be represented as,

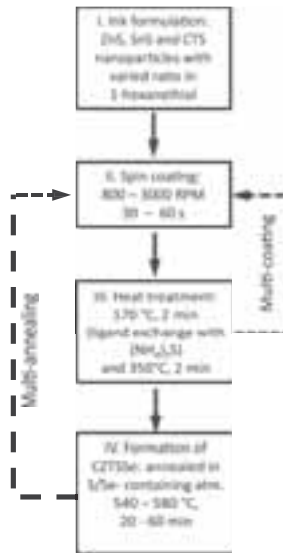
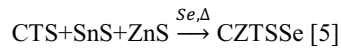


Figure 1: Preparation process of NP based CZTSSe absorber layers[5]

Metal salt based CZTS ink were prepared by mixing Copper chloride, zinc acetate dihydrate, tin chloride dehydrate, thiourea and sodium fluoride in 12 mL DMSO with stirring overnight. The metal ratios of the ink precursor were Cu/(Zn+Sn) = 0.73 and Zn/Sn = 1.02. NaF was directly introduced in the Cu-Zn-Sn-S ink with a concentration of 0.14 M. The resulting ink is well adapted for inkjet printing as revealed by the measurement of the contact angle. The best inkjet printing condition was found by adjusting the printing parameters (droplet volume less than 20 pl., printing speed set to 4.8 to 7.2 m/min). The resolutions in both

the X and Y directions for the printing were 400 dpi. With such conditions, the volume of ink needed for each printing on an 25.4 mm x 25.4 mm substrate is calculated to be less than 4  $\mu\text{L}$ . Figure 2 shows the prepared ink and operating principle of inkjet printing. The as-deposited Cu-Zn-Sn-S precursor layers after printing were baked to remove the residual solvent on a pre-heated hot plate at 300  $^{\circ}\text{C}$  for 2 min. A second annealing in selenium containing atmosphere at 560  $^{\circ}\text{C}$  for 20 min allow the formation of well crystallized CZTSSe thin film absorbers.



Figure 2: Formulated ink and operation principle of inkjet printing.

## 2.2 Fabrication of solar cells

Solar cells were fabricated by chemical bath deposition of a CdS buffer layer, and subsequently by sputtering of i-ZnO and aluminum doped ZnO window layers. A Ni/Al upper contact electrode was deposited by evaporation using a shadow mask. Finally solar cells with an area of 0.5  $\text{cm}^2$  were defined by mechanical scribing. The fabricated Solar cells with Mo/CZTSSe/CdS/i-ZnO/ZnO:Al/Ni:Al grids were studied for their photon conversion efficiency.

## 2.3. Characterization

X-ray diffraction (XRD) was used to verify the crystalline structure of NP and metal salt based CZTSSe absorber layers. Bruker D8-Advance X-Ray diffractometer was used with Cu  $K_{\alpha}$  radiation in a step size of 0.02 $^{\circ}$  and a step time of 5s. The contact angle was measured by using “contact angle system OCA” from data physics Instruments GmbH, Germany. The SEM image was recorded in a LEO 1530 GEMINI SEM of Zeiss at an acceleration voltage of 10 kV. Solar cell efficiency was calculated from J-V curves under 1.5 AM, 100  $\text{mW cm}^{-2}$  illumination by using an in-house class A sun simulator.

## 3. Results and Discussion

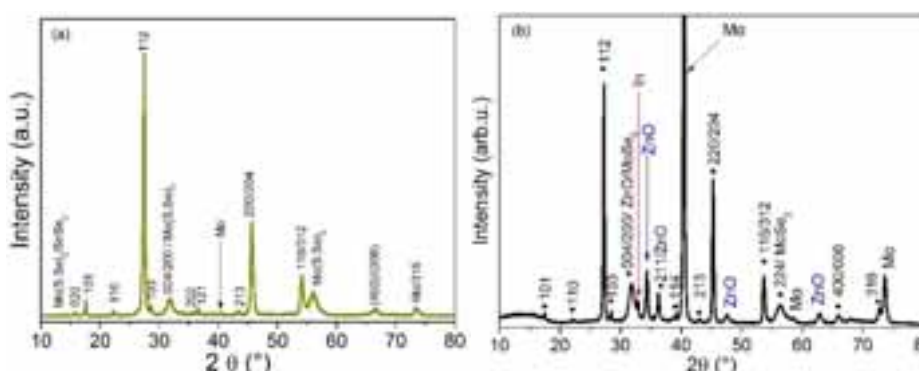


Figure 3: XRD patterns of (a) a NP based CZTSSe thin film and (b) metal salt based CZTSSe device.

XRD pattern in figure 3 (a) shows tetragonal structure for NP based CZTSSe sample. There are peaks from the Mo substrates as well. Peaks corresponding to Mo(S,Se)<sub>2</sub> are also observed. Usually Zn(S,Se) and CTS crystallographic peaks overlap with CZTSSe peaks, and it is difficult to identify the exact phase. It has been verified that there is no separate phase such as ZnS and CTS exist in CZTSSe using Raman spectroscopy (data is not shown here). Figure (3) (b) displays the XRD pattern of the metal salt based CZTSSe completed

device. Peaks assigned to CZTSSe are indexed as shown in the Figure. Since the measurement was performed on complete device, peaks related to window layer of ZnO and Mo substrate were also detected.

Figure 4 shows the contact angle of DMSO before (Figure 4a, 21.6°) and after adding Cu, Zn, and Sn metal salts (Figure 4b, 42.4°), which conform with the increase of the viscosity with increasing metal salts concentration. For the metal ratio used in this study ( $\text{Cu}/(\text{Zn}+\text{Sn})=0.73$  and  $\text{Zn}/\text{Sn}=1.02$ ), the contact angle still below 90° suggesting the feasibility for the formation of a homogeneous film on Mo substrate by inkjet printing [12].



Figure 4: Contact angle of (a) DMSO and (b) formulated ink containing Cu-Zn-Sn-S precursor on Mo coated glass substrate.

Figure 5a shows the cross sectional scanning electron microscopy (SEM) image of NP based CZTSSe with a thickness of around 4.5  $\mu\text{m}$ . It is a four layered structure with fine grain/large grain/fine grain/large grain arrangement on top of Mo layer. Device geometry is not shown here. The SEM image in Fig. 5b shows a complete metal salt route based CZTSSe device. Crack free compact CZTSSe is synthesized as shown in Fig.5b [12]. A layer of  $\text{MoSe}_2$  is formed in-between the Mo layer and CZTSSe absorber layer due to the reaction between Mo and chalcogen Se (during selenisation). Generally, a thin  $\text{MoSe}_2$  layer is helpful in adhesion and provides an Ohmic contact for the  $\text{Cu}(\text{In,Ga})\text{Se}_2$  (CIGS) solar cells [13]. These findings could be also applied to CZTSSe solar cells due to the similar properties between CZTS and CIGS. However, an excessively thick  $\text{MoSe}_2$  layer may have adversely effect on the performance of CZTSSe solar cells because of the high resistance of lead to a high series resistance of  $\text{MoSe}_2$  layer (in the range of  $10^1$  to  $10^4 \Omega\cdot\text{cm}$  [14]).

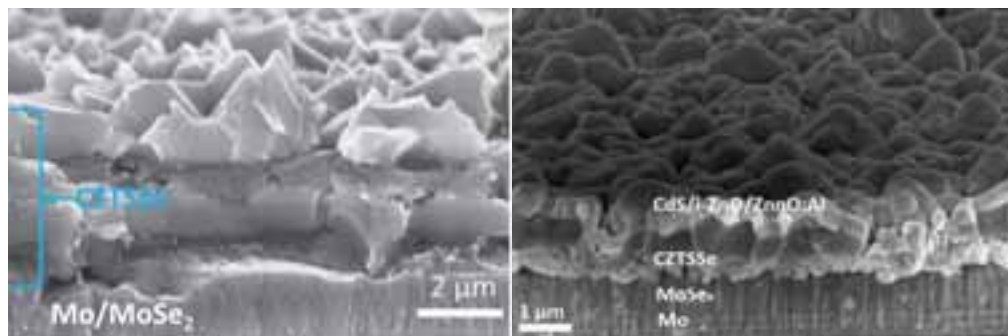


Figure 5: Cross-sectional scanning electron micrograph of NP based CZTSSe thin films (left) and the complete solar cell based on metal based CZTSSe (right).

The corresponding I-V characteristics measured in the dark and under AM 1.5 conditions are shown in Figure 6. The curves in blue show typical J-V curves of NP based CZTSSe solar cell under dark and illumination. Conversion efficiency of 3.0 % was achieved with an open circuit voltage ( $V_{oc}$ ) of 306.5 mV, short circuit current density ( $J_{sc}$ ) of 27.5  $\text{mA}/\text{cm}^2$ , and fill factor (FF) of 35.0 %.

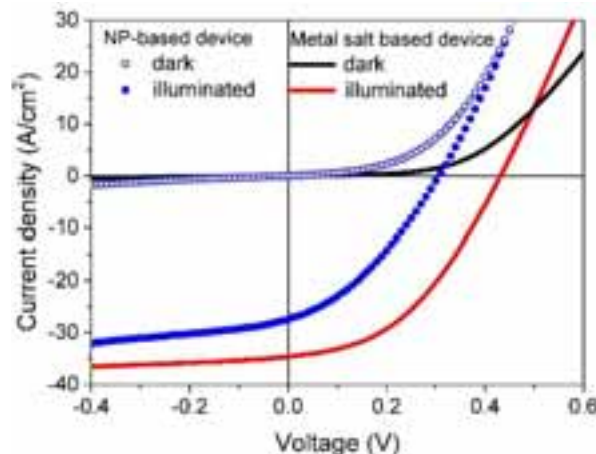


Figure 6: J-V characteristics in the dark and under illumination measured under AM 1.5 conditions for NP based CZTSSe device and metal salt based CZTSSe device. The area of the device is  $0.5 \text{ cm}^2$ .

Compared to spin coating method where most of the ink dropped on to spin coater substrates are spun away during rotation, inkjet printing method allows a uniform deposition with a negligible material waste due to the drop on demand properties. This reduces the material waste and cost of the solar cell. For example, in one of our studies,  $20 \mu\text{l}$  ink is enough for the deposition of  $1 \mu\text{m}$  thick absorber film in an  $\text{inch}^2$  area [12]. Moreover, solar cells prepared with  $0.5 \text{ cm}^2$  area in a glass/Mo/CZTSSe/CdS/ZnO structure demonstrated a power conversion efficiency of 6.4% (J-V curve in red in Figure 6). The  $V_{\text{OC}}$  was 431 mV,  $J_{\text{SC}}$  was  $34.6 \text{ mAcm}^{-2}$ , and fill factor FF was 42.8%. The series resistance, shunt resistance, and diode quality were found to be 5.7,  $1230 \Omega \text{ cm}^2$ , and 2.3, respectively, by fitting the dark  $J-V$  curve using one diode model.

The device performance is mainly limited by the low fill factor, which could be due to the high series resistance. Several factors may contribute to the high series resistance. One of the reason could be the thick  $\text{MoSe}_2$  at the back contact. Another reason could be the fine grain layers near the back contact. We do not have a direct proof for that at the moment. Further studies are needed. The defect level studies on the CZTSSe thin films by photoluminescence (PL) and surface photovoltage spectroscopy (SPV) shows an increased  $(\text{Zn}_{\text{Cu}})^+$ ,  $[\text{Zn}_{\text{Sn}}+\text{Cu}_{\text{Zn}}]$  defect states and a dominating quasi donor-acceptor pair recombination in the recombination process [15]. We know the samples studied are Cu poor and Zn rich and the Cu and Zn disorder is already observed in the neutron diffraction studies as well [16]. This could also be a reason affecting the performance of the solar cell.

#### 4. Conclusion and Outlook

Nanoparticle inks are affected by stability issues which is due to the agglomeration of NPs after certain time. To avoid this agglomeration long chain organic-ligand is used during the formation of ink. However, it is difficult to remove the long chain organic ligand which stabilizes the NPs completely from the thin films. A combination of ligand exchange and non-ligand exchange processes result a crack free CZTSSe absorber film. Selenisation lead to a layered structure with unwanted carbon in the grains. The carbon serves as a barrier for the growth of NP, however gives an efficiency around 1-3% [5]. we explored DMSO as solvent for the formulation of stable Cu-Zn-Sn-S precursor ink and by varying the concentration of Cu, Zn, and Sn metal salts, the viscosity can be controlled. The resulting ink is well adapted for inkjet printing as revealed by the measurement of the contact angle. Inkjet printing is more effective than the spin coating in terms of raw material utilization. Solar cells with glass/Mo/CZTSSe/CdS/ZnO structure with total area ( $0.5 \text{ cm}^2$ ) power conversion efficiency of 6.4% are demonstrated from thin film absorbers processed by inkjet printing technology of Cu-Zn-Sn-S precursor ink followed by selenisation. Inkjet printing allows the development of

Micro concentrator solar cell concept, which allows enhancing the efficiency of PV devices while reducing the material consumption. Furthermore, the adaptation and integration of micro-lenses for optimal concentration of light on micrometer size solar cell is a promising area of interest which can use micro-CPV with integrated optics without the need of tracking system.

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